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(54) **Organometallic complexes of aluminium, gallium and indium**

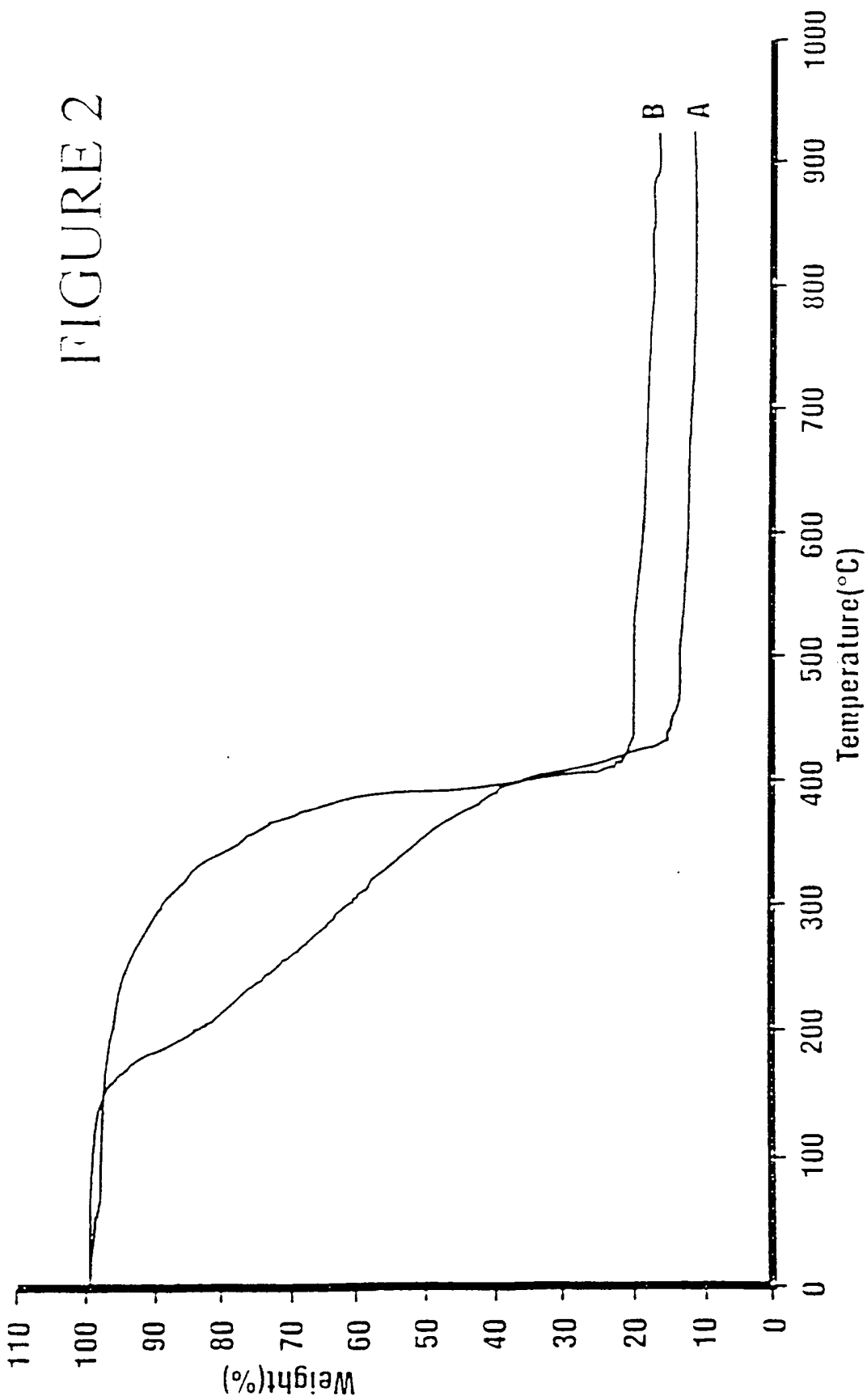
(57) Novel organometallic complexes of aluminium, gallium and indium are disclosed, having improved stability and volatility for use in CVD processes. These are donor ligand complexes of the formula ML_3 where M is the metal, and L is a ligand containing an amidine ($R'N-C(R')-NR'$) group, where R' is H, alkyl etc.

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At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

FIGURE 2



where M is aluminium, gallium or indium; and L is an organic ligand containing a substituted or unsubstituted amidino $[R'N\equiv C(R')\equiv NR']$ group.

5 The advantages of the complexes of the present invention are that they are more stable to air and moisture. Moreover, they reduce the levels of residual, unwanted alkyl groups during and after CVD processes.

The reduced alkyl content of the complex of the present invention also reduces significantly the possibility of carbon inclusion in the deposited product.

10 Furthermore, the complex of the present invention has a distinct advantage over the acetylacetonato analogues which are typically used in MOCVD in that the highly preferred complexes of the present invention contain no oxygen, the presence of which is detrimental to film formation. In this regard, AcAc gives Ga_2O_3 .

15 Preferred amidine ligands are amidines of the formula II:



20 where R' is H, C_1-C_8 alkyl or haloalkyl, C_3-C_8 cycloalkyl, optionally including an -NH- group in the ring, C_3-C_8 cycloalkenyl, phenyl or substituted phenyl containing from 1-3 (C_1-C_8)alkyl or halo-substituents, trimethylsilyl or halogen, the R' groups being the same or different.

25 Typical amidine ligands within that formula are N,N'-diphenylbenzamidine, N,N'-di(p-chlorophenyl)acetamidine, N,N'-diphenylformamidine, N,N'-di(p-fluorophenyl)acetamidine, benzamidine, acetamidine, and N,N'-dicyclohexylacetamidine. Other suitable amidine ligands will be apparent to those skilled in the art, as will be methods for the preparation of such amidines.

30 The amidine complexes of this invention are prepared by reacting a suitable amount of the trialkylaluminium, trialkylgallium or trialkylindium compounds, e.g.

and the resulting white suspension was heated under reflux for 12 hours, giving a flocculent pale yellow suspension. The solvent was removed under vacuum to give a pale green/yellow solid which was dissolved in a minimum quantity of chloroform and recrystallised by cooling to -35°C , producing a slightly air sensitive pale green powder.

Yield: 62%

Found: C, 79.97; H, 5.59; N, 9.55%

$\text{C}_{57}\text{H}_{45}\text{N}_6\text{Al}$ requires C, 80.86; H, 5.55; N, 10.30%

^1H NMR (CDCl_3) 7.20 (ArH, 3H, t, 7Hz), 7.09 (ArH, 6H, t, 7Hz), 7.00 (ArH, 12H, t, 8Hz), 6.86 (ArH, 12H, t, 7Hz), 6.64 (ArH, 12H, d, 7Hz).

HRMS(EI): calcd for $\text{C}_{57}\text{H}_{45}\text{N}_6\text{Al}$ (M)⁺ m/z 840.342112, found m/z 840.352 + 0.0016 MS (EI) m/z 840 (M⁺, 6%), 56([M-PhNCPhNPh]⁺, 23%), 272([LH]⁺, 10%), 180([M-(PhNCPhNPh)₂AlNPH]⁺), 100%.

Synthesis of $\{\text{Ga}(\text{NPhCPhNPh})_3\}$

N,N'-Diphenylbenzamidine (0.95g, 3.5 mmol) and monomethylgalliumbis(N,N'-diphenylbenzamidine) (2.19g, 3.5mmol) were dissolved in a sealed tube and heated to 200°C for 30 mins, over which time methane (1 mole equivalent) was evolved. The pale yellow solid was dissolved in chloroform (15cm^3), and the solution cooled to -35°C , producing slightly air sensitive pale yellow crystals. These were isolated by removing the solvent by filtration and washed with hexane ($2 \times 10\text{cm}^3$), and dried in vacuum.

Yield 2.0g (65%)

Found: C, 77.10 H, 5.25, N, 9.40

$\text{C}_{57}\text{H}_{45}\text{N}_6\text{Ga}$ requires C, 77.47, H, 5.13, N, 9.51.

$C_{42}H_{39}N_6$ In requires C, 73.71; H, 4.88; N, 9.05%.

Found: C, 74.44; H, 4.81; N, 8.83%.

1H NMR ($CDCl_3$): δ /ppm 6.56 (d, 12H, o-ArH-N), 6.80 (t, 6H, p-ArH-N), 6.94 (t, 12H, m-ArH-N), m 7.01-7.05 (d, 6H, p-ArH-C), 7.11-7.26 (m, 9H, o-ArH-C, m-ArH-C).

Crystals of this compound suitable for x-ray diffraction were grown and characterisation by x-ray crystallography establishes the structure of the complex to be monomeric and to contain three bidentate amidinato groups, as shown in Figure 1 of the accompanying drawings.

Synthesis of $[Al(PhNCMeNPh)_3]$

This complex was prepared using the same procedure as used for aluminium-tris(*N,N*-diphenylbenzamidinato). A solution of Al_2Me_6 in hexanes (0.79cm³, 0.79mmol) was added to a suspension of *N,N'*-diphenylacetamidine (1.0g, 4.76mmol) in hexane. The product is a colourless crystalline solid.

Yield: 0.82g (79%).

$C_{42}H_{39}N_6$ Al requires C, 77.04; H, 6.00; N, 12.83%.

Found: C, 76.56; H, 6.09; N, 12.62%.

1H NMR ($CDCl_3$): δ /ppm 2.00 (s, 9H, CH_3), 6.73 (d, 12H, o-ArH-N), 6.99 (t, 6H, p-ArH-N), 7.18 (t, 12H, m-ArH-N).

Synthesis of $\{In(PhNCMeNPh)_3\}$

N,N'-Diphenylacetamidine (0.53g, 2.52mmol) was reacted with ethylindium-bis(*N,N'*-diphenylacetamidinato) (1.42g, 2.25mmol) in a sealed tube at 180°C and the product washed with hexane (2 x 10cm³). The product is a colourless solid.

CLAIMS:

1. Organometallic aluminium, gallium and indium complexes of the formula I:



wherein

M is aluminium, gallium or indium; and

10 L is an amidino group of the formula II



wherein

15 R' is H, C₁-C₈ alkyl or haloalkyl, C₃-C₈ cycloalkyl optionally including an NH- group in the ring, C₃-C₈ cycloalkyl, phenyl, substituted phenyl containing from 1-3 (C₁-C₅) alkyl or halo-substituents, trimethylsilyl or halogen, the R' groups being the same or different.

- 20
2. Organometallic aluminium, gallium and indium complexes according to claim 1 wherein the amidine group is derived from any one of the following: acetamidine, benzamidine, N,N'-diphenylbenzamidine, N,N'-di(p-chlorophenyl)-acetamidine, N,N'-diphenylformamidine, N,N'-diphenylacetamidine, N,N'-di(p-tolyl)benzamidine, 25 N,N'-di(p-fluorophenyl)acetamidine, and N,N'-dicyclohexylacetamidine.

- 30
3. A method for the chemical vapour phase deposition of aluminium, gallium or indium on a substrate which comprises contacting the substrate with a volatile organometallic gallium or indium in the vapour phase, wherein there is used an organometallic aluminium, gallium or indium complex according to claim 1 or claim 2.



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Application No: GB 9523981.0
Claims searched: 1-3

Examiner: Roy Honeywood
Date of search: 31 January 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK CI (Ed.O): C2C (CNA)

Int CI (Ed.6): C07F

Other: ONLINE: CAS

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
	None	

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.